

INFLUENCE OF COAL TYPE AND PYROLYSIS TEMPERATURE ON SULFUR DISTRIBUTION IN PRODUCTS DURING DEVOLATILIZATION

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ABSTRACT

During coal devolatilization, the coal sulfur is distributed into solid, liquid, and gaseous products depending on the type and quantity of the coal sulfur and the processing conditions (e.g., temperature, pressure, and heating rate) used. In this study, a series of coals was devolatilized at a relatively low temperature in a fixed-bed reactor in an inert atmosphere. The distribution of sulfur in solid, liquid, and gaseous products was monitored. Influence of peak devolatilization temperature on sulfur distribution in products was determined for a high-volatile bituminous coal (Pittsburgh No. 8). The sulfur content of the pyrolysis liquids generated at 500°C correlate well with the total coal sulfur. The total sulfur of the char can be correlated with the pyritic sulfur content of the coal. Total gaseous sulfur content (sum of H_2S and COS) increases with the increase in pyritic or organic sulfur of coal but direct correlations are poor. An increase in pyrolysis temperature increases the total gaseous sulfur yield. Based on sulfur distribution data for about 25 coals, models have been developed to correlate the sulfur yield in products with the total sulfur of the feed coal.

INTRODUCTION AND OBJECTIVES

A fundamental understanding of the physical and chemical transformations of coal sulfur which occur during pyrolysis is essential for effective utilization of the large reserve of coal available in the United States (1). Work at the Morgantown Energy Technology Center (METC) demonstrated that a relatively high-quality liquid fuel (low sulfur, high H/C) can be produced by low-temperature devolatilization of coal (2,3). Coal devolatilization is a key step in various conversion processes including gasification, combustion, and liquefaction. The organic and inorganic constituents of coal (including sulfur) undergo significant changes during devolatilization. The extent of these changes depend on the peak pyrolysis temperature, heating rate, gas atmosphere, and most importantly, coal type. The objective of this study was to investigate the distribution of coal sulfur into gaseous, liquid, and solid products that occurs during devolatilization of coal of various types.

BACKGROUND

Influence of Coal Type on Sulfur Evolution

Numerous factors influence the mechanisms of sulfur release during the pyrolysis of coals of various types. Some excellent reviews on the sulfur chemistry of coal are available (4-11). However, with the exception of a few limited studies (10,12,13), relatively little has been reported on the influence of coal type on sulfur release during devolatilization, especially at relatively low temperatures (500 to 600°C). This temperature region is where significant changes in coal structure occur. Furthermore, very few correlations between the sulfur in coal and its distribution in the products and evolution rates are available in the literature.

It is generally accepted that three forms of sulfur occur in coal (8,14): (a) organic sulfur (an integral part of coal structure), (b) pyritic and/or marcasites (generally discrete particles or "lumps"), and finally, (c) sulfates (as salts of calcium or iron). Sulfates are not usually present in large quantities in raw

coal. However, significant amounts can be formed if the coal has been weathered (i.e., oxidized). The type and distribution of organic sulfur vary widely in a complex manner in different coals. Roughly 40 to 70 percent of the organic sulfur of a coal is in thiophene structure (and its derivatives). The remaining 30 to 60 percent is present as thiols (R-SH), sulfides (R-S-R'), and disulfides (R-S-S-R'). Thiophenes are hetero-aromatic compounds with the sulfur as part of an aromatic ring. In an aryl sulfide, the sulfur is linked to an aromatic ring. In cyclic sulfides, the sulfur is part of a nonaromatic ring. Sulfides are usually present as aryl sulfides, cyclic sulfides, and aliphatic sulfides in a ratio of 3:2:1, respectively (5,6). For high-rank coals, disulfides are not believed to be a significant portion of the total sulfur (5). The amount of thiols is substantially higher in lignites and high-volatile coals than in low-volatile coals (5). The coalification process appears to cause the organic sulfur to change from -SH through R-S-R' to thiophene by cyclization reactions. In summary, the bonding of the organic sulfur with the coal structure varies with the coal rank. The greater rigidity of sulfur present in the higher rank coals renders the sulfur more stable during heat treatment.

The amount of volatile matter evolved during pyrolysis also influences the sulfur evolution process (12). The volatile matter yield of the lower rank coals (hvAb or lower) is significantly higher than that of the higher rank coals. The lower rank coals with higher volatile matter content will retain less sulfur in the residue (by fixation of sulfur by organic or inorganic coal constituents) than the higher rank coals. Finally, the indigenous mineral matter present in coal (particularly calcium and iron compounds) may react and fix sulfur species in the solids during devolatilization.

Transformation of Coal Sulfur During Heat Treatment

The pyrite present in a coal decomposes to ferrous sulfide and sulfur when heated in an inert atmosphere by the following reaction: $\text{FeS}_2 \longrightarrow \text{FeS} + \text{S}$ (Reaction 1, Table 1). This transformation begins at 450 to 500°C and is essentially complete at 850°C. At elevated temperatures, the pyrite may be reduced by carbon (Reaction 3 of Table 1). Examples of reactions of pyrite with hydrogen (donated by coal), CH_4 , or CaSO_4 are shown by the Reactions (4), (5), and (6), respectively (Table 1).

Most aliphatic sulfur compounds decompose appreciably at about 500°C. Diethyl sulfides begin decomposition at ~400°C to form H_2S and mercaptans. Aliphatic and benzylic sulfides, mercaptans, and disulfides lose H_2S between 700 and 800°C. Aromatic sulfides and mercaptans are relatively stable (5) and yield H_2S and CS_2 only at a relatively high temperature (800°C). Examples of the reactions of organic sulfur are summarized in Table 1.

Yergey, et al. (15), performed nonisothermal kinetic studies on sulfur evolution in hydrogen at a relatively slow heating rate (1 to 100°C/min). They developed a kinetic scheme to describe the H_2S evolution in hydrogen. Stinnet, et al. (16), applied the principle of free energy minimization and used the NASA chemical equilibrium code (CEC) to predict the composition of the fixed-bed exit gases, including the sulfur species. In 1932, Snow (13) investigated the conversion of coal sulfur at various peak temperatures in the presence of different gases and reported that first traces of H_2S could be observed at a temperature as low as 200°C. Calkins (10) studied the conversion of coal and model organic sulfur in a rapidly heated fluid-bed reactor.

EXPERIMENTAL


A fixed-bed reactor (slow heating rate organic devolatilization reactor, SHRODR) was used to generate pyrolysis liquids at 500° C. More details on this reactor system and the experimental procedures are available (2,3). A range of feedstocks (primarily coal, but also oil shale, and tar sand) was devolatilized in this reactor. In this study only the coal data were considered. Most coal samples were supplied by


TABLE 1. A Summary of Possible Reactions Involving Sulfur Compounds During Coal Devolatilization

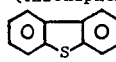
Inorganic

- $\text{FeS}_2 \xrightarrow[500^\circ\text{C}]{\text{inert}} \text{FeS} + \text{S} \longrightarrow \text{Nonvolatile S Compounds}$ (1)
- \downarrow
 $(\text{coal-H}) \longrightarrow \text{H}_2\text{S} + (\text{coal})$ (2)
- $\text{FeS}_2 \xrightarrow[1,000^\circ\text{C}]{(\text{coal C})} \text{CS}_2 + 2 \text{FeS} + (\text{Coal}) \longrightarrow 2 \text{Fe} + \text{CS}_2$ (3)
- $2 \text{FeS}_2 \xrightarrow[230^\circ\text{C}]{\text{H}_2} \text{Fe}_2\text{S}_3 + \text{H}_2\text{S} \xrightarrow[280^\circ\text{C}]{\text{H}_2} 2 \text{FeS} + 5 \text{H}_2\text{S} \xrightarrow[370^\circ\text{C}]{\text{H}_2} 2 \text{Fe} + 2 \text{H}_2\text{S}$ (4)
- Similar Reactions are possible between CO and FeS_2
- $4 \text{FeS}_2 + \text{CH}_4 \xrightarrow[500^\circ\text{C}]{} \text{CS}_2 + 4 \text{FeS} + 2 \text{H}_2\text{S}$ (5)
- $\text{CaSO}_4 + \text{FeS}_2 + \text{H}_2\text{O} \longrightarrow \text{CaO} + \text{FeS} + 2 \text{SO}_2 + \text{H}_2$ (6)

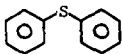
Organic

-  $\xrightarrow[>450^\circ\text{C}]{\text{H}_2} \text{C}=\text{C}-\text{C}=\text{C} + \text{H}_2\text{S} \xrightarrow{\text{H}_2} \text{C}_4\text{H}_{10} + \text{H}_2\text{S}$ (7)
- (Thiophene)

-  $\xrightarrow[500^\circ\text{C}]{\text{H}_2} \text{Thionaphthene} \xrightarrow{\text{H}_2} \text{H}_2\text{S} + \text{C}_6\text{H}_5\text{C}_2\text{H}_5 + \text{C}_6\text{H}_5\text{C}_2\text{H}_7$ (8)
- (Thionaphthene)

-  $\xrightarrow[>550^\circ\text{C}]{\text{H}_2} \text{Dibenzothiophene} + \text{H}_2\text{S}$ (9)
- (Dibenzothiophene)

- $\begin{array}{c} \diagup \quad \diagdown \\ \text{C} \quad \text{C} \\ || \quad || \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{HH} \end{array} + \text{H}_2\text{S} \longrightarrow \begin{array}{c} \diagup \quad \diagdown \\ \text{C} \quad \text{C} \\ || \quad || \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{S} \end{array} + 2 \text{H}_2$ (sulfur fixation reaction) (10)

-  $\longrightarrow \text{Dibenzothiophene} + \text{H}_2$ (cyclization reaction) (11)
- Diphenyl Sulfide Dibenzothiophene

the Penn State/DOE coal data bank (17). Sample preservation and avoidance of air oxidation of the samples were key considerations in this investigation as reported previously (18-22). Availability of fresh (well-preserved, not weathered) samples was the criterion used for sample selection. Some coal samples utilized by Given, et al. (22), for an investigation on direct liquefaction were selected in this study for comparison with our pyrolysis studies. Primarily bituminous coals were used in this study as these are known to yield the highest liquid product during pyrolysis (1,2). All samples were prepared and handled in an inert atmosphere.

About 25 coal samples, mostly in the high-volatile range, were investigated in this study. The carbon content of the samples ranged between 70 and 80 percent (daf) while the oxygen content ranged from less than 2 to over 20 percent. The sulfur content of these coals varied widely from < 0.5 to over 6 percent (of dry coal). The sulfur type in the feedstocks and the distribution of the sulfur in selected products are provided in Table 2. The Statistical Analysis System (SAS) program developed by the SAS Institute (24) was used for data analysis.

RESULTS AND DISCUSSION

Influence of Coal Type on Sulfur Distribution in Products

A summary of the distribution of coal sulfur to the gaseous, liquid, and solid products resulting during pyrolysis at 500°C is presented by the following equations:

$$\text{Total sulfur in gas} = 0.31 \times S_{\text{coal}} \quad [R^2 = 0.93, F = 425, P = 0.0001] \quad (1)$$

$$\text{Total sulfur in tar} = 0.06 \times S_{\text{coal}} \quad [R^2 = 0.85, F = 175, P = 0.0001] \quad (2)$$

$$\text{Total sulfur in solid} = 0.61 \times S_{\text{coal}} \quad [R^2 = 0.98, F = 1476, P = 0.0001] \quad (3)$$

The above correlations show that for our data set, about 61 percent of the coal sulfur appears in the char while 31 percent of the coal sulfur appears in the gaseous products (sum of H₂S and COS). Only a small portion of the coal sulfur (6 weight percent) evolve as the total sulfur of the pyrolysis liquids. This is partly because a relatively small portion of coal (5 to 25 percent) is converted to liquids during pyrolysis. The water evolved during pyrolysis contains relatively insignificant amounts of dissolved sulfur species.

The R², F- and P-values for the models are also summarized with the equations. R², the coefficient of determination, measures how much of the variation in the dependent variable can be attributed to the model (i.e., independent variable), rather than to random error. R² has been calculated using the regression program of SAS (R² for the no-intercept version was redefined by SAS, Reference 24).

The F-value is the ratio of the mean square for the model divided by the mean square error. It is a test of how well the model as a whole (after adjusting for the mean) accounts for the behavior of the dependent variable. P is the significance value or probability of obtaining at least as great an F value, given that the hypothesis is true. When P < 0.05, the effect is usually termed "significant." For more details on these statistical terms, see Reference 24.

The total gaseous sulfur yield (i.e., sum of H₂S and COS), the major gaseous sulfur products evolved during pyrolysis of coal, can be correlated with the feed dry coal sulfur (Figure 1A). The solid line represents the regression fit through the data. The dotted lines represent 90th percentile confidence limits for the mean predicted values.

TABLE 2. Sulfur Contents of the Coals and the Distribution of the Sulfur in Products (Tar, Char, and Gases)

Coal	Rank	Sulfur Content, Coal				Products			
						(Wt. %, Dry)		(Wt. %, Dry)	
		Total	Pyritic	Organic	Sulfate	Tar	Char	Coal	
						Total	Total	H ₂ S	COS
PSOC 123	hvAb	0.68	0.06	0.61	0.01	0.72	0.45	0.201	0.035
PSOC 181	SubA	0.58	0.04	0.54	0.00	0.54	0.45	0.067	0.025
PSOC 267	hvAb	1.96	0.02	1.89	0.05	0.78	1.00	0.487	0.096
PSOC 275	hvAb	2.14	1.41	0.73	0.00	1.17	2.46	0.503	0.098
PSOC 296	hvAb	0.98	0.91	0.07	0.00	0.73	0.91	0.436	0.034
PSOC 306	hvAb	2.05	1.21	0.83	0.01	1.54	1.72	0.559	0.083
PSOC 355	hvAb	2.77	2.12	0.63	0.02	1.02	2.27	0.605	0.177
PSOC 375	hvAb	1.11	0.38	0.68	0.05	0.90	1.20	0.415	0.060
PSOC 1109	hvCb	1.82	0.78	0.71	0.33	0.75	2.02	0.348	0.073
PSOC 1313	mvb	5.65	4.52	0.98	0.51	2.57	4.23	1.040	0.231
PSOC 1323	hvBb	4.10	1.47	2.29	0.34	2.39	3.10	1.491	0.216
PSOC 1448	hvAb	0.46	0.04	0.41	0.01	0.22	0.36	0.190	0.028
PSOC 1449	hvAb	1.64	0.53	1.09	0.02	0.55	2.08	0.560	0.103
PSOC 1469	hvAb	0.79	0.26	0.51	0.02	0.46	0.56	0.236	0.051
PSOC 1470	hvAb	2.50	1.88	0.58	0.04	--	--	--	--
PSOC 1471	hvAb	1.04	0.22	0.79	0.03	0.55	0.73	0.468	0.074
PSOC 1472	hvAb	0.85	0.28	0.55	0.02	0.38	0.62	0.406	0.031
PSOC 1473	hvAb	0.63	0.08	0.53	0.02	0.30	0.49	0.207	0.025
PSOC 1475	hvAb	0.98	0.32	0.64	0.02	0.41	0.67	0.300	0.049
PSOC 1481	hvAb	4.82	3.20	1.42	0.20	2.10	3.88	1.061	0.248
PSOC 1492	hvCb	4.35	1.82	2.50	0.03	2.24	3.20	1.325	0.222
PSOC 1499	hvAb	0.67	0.02	0.65	0.00	0.34	0.53	0.278	0.061
PSOC 1502	hvCb	0.51	0.15	0.36	0.00	0.25	0.40	0.229	0.051
PSOC 1504	hvAb	0.77	0.04	1.21	0.02	0.41	0.54	0.284	0.088
PSOC 1517	hvAb	1.92	0.70	1.21	0.01	0.41	1.89	0.779	0.131
PSOC 1520	SubC	1.21	0.05	1.15	0.01	0.50	1.08	0.401	0.043
PSOC 1523	hvAb	0.71	0.02	0.69	0.00	0.53	0.48	0.373	0.054
PSOC 1524	hvAb	1.85	1.39	0.44	0.02	0.81	1.81	0.571	0.046
PITT No. 8	hvAb	1.99	0.34	1.08	0.13	0.72	1.77	0.359	0.067
OHIO No. 6	hvCb	2.91	--**	--	--	0.88	2.46	0.462	0.229
WELLMORE No. 8	hvAb	1.23	--	--	--	0.43	0.95	0.507	0.051
AMAX*	hvAb	0.91	--	--	--	0.35	0.58	0.316	0.038

* Physically/chemically cleaned by AMAX process. Kentucky Hazard coal.

** Not available.

A single, variable model (total coal sulfur) was used to predict the sulfur yield. The predicted and experimental H_2S and COS are compared in Figures 1B and 1C. The following equations describe the yields of these gaseous species:

$$[H_2S] = S_{\text{coal}} \times 0.259 \quad [R^2 = 0.91, F = 319, P = 0.0001] \quad (4)$$

$$[COS] = S_{\text{coal}} \times 0.050 \quad [R^2 = 0.94, F = 504, P = 0.0001] \quad (5)$$

In these equations $[H_2S]$ and $[COS]$ signify weight percent of coal sulfur as H_2S and COS in the products. The combined amount represented by Equations 4 and 5 agrees with the amount represented by Equation 1. Additional two-variable models (including the total sulfur and organic sulfur) facilitated improved predictions of the experimental results. These results will be discussed in a separate communication.

The sulfur content of the pyrolysis tar (weight percent) can be predicted based on the coal sulfur (weight percent dry coal) as shown in Figure 2A. The following equation describes this prediction:

$$S_{\text{tar}} = 0.467 \times S_{\text{coal}} \quad [R^2 = 0.946, F = 522, P = 0.0001], \quad (6)$$

where S_{tar} equals weight percent sulfur in tar, and S_{coal} equals weight percent sulfur in dry coal.

The finding shows that the pyrolysis liquids contain less than half as much sulfur as the parent coal (for the same amount of fuel by weight).

The correlations between the pyritic, organic, or sulphatic sulfur in the coal and the sulfur content of the tar were poor.

The char sulfur (weight percent char) can be correlated with the sulfur content of the parent coal (weight percent dry coal), as shown in Figure 3A. The total char sulfur content (weight percent of char) can be correlated somewhat with the pyritic sulfur content of the parent coal (Figure 3B). The greater the pyritic sulfur content of the coal, the larger the char sulfur. From a thermodynamic standpoint, pyrite is unstable above 450°C . Not all pyrite is decomposed at 500°C even when a long residence time (~ 40 min) is maintained at a temperature above the pyrite decomposition temperature. This finding suggests that the kinetics of pyrite decomposition and reaction strongly influences the amount of sulfur liberation. The sulfur content of the char can be predicted based on the feed coal sulfur (dry basis). The following equation represents this relationship:

$$S_{\text{char}} = S_{\text{coal}} \times 0.81 \quad [R^2 = 0.975, F = 1192, P = 0.0001], \quad (7)$$

where S_{char} = sulfur content of char (weight percent), and S_{coal} = sulfur content of coal (weight percent).

Influence of Peak Pyrolysis Temperature on Sulfur Distribution in Products

To investigate the influence of the peak devolatilization temperature on sulfur evolution during coal pyrolysis, Pittsburgh No. 8 coal was pyrolyzed to various peak temperatures. Data on the influence of the peak pyrolysis temperature on product distribution and quality have been reported (2,3). This coal contained about 2 weight percent sulfur (dry basis). The correlation coefficient between the total gaseous sulfur content (summation of COS and H_2S , expressed as the weight percent of dry feed coal sulfur) with the pyrolysis temperature (between 400 and 725°C) was 0.99 (Figure 4). The general regression model [GLM] of SAS provided the following relationship on sulfur yield for the temperature range 400 to 725°C :

$$\text{Total S in gas} = (0.00103) \times (\text{Temp, in}^\circ\text{C}) \quad [R^2 = 0.99, F = 234, P = 0.0006] \quad (8)$$

An increase in temperature resulted in an increase in the sulfur content of the tar (expressed as weight percent of the feed dry coal sulfur). As one would expect, the total and pyritic sulfur content of the char decreased as the peak heat treatment temperature increased. In contrast, the char organic sulfur content increased (data not shown) with an increase in the heat treatment temperature. The influence of peak pyrolysis temperature or heating rate on the sulfur distribution in products for additional coals will be addressed in future studies.

SUMMARY AND CONCLUSIONS

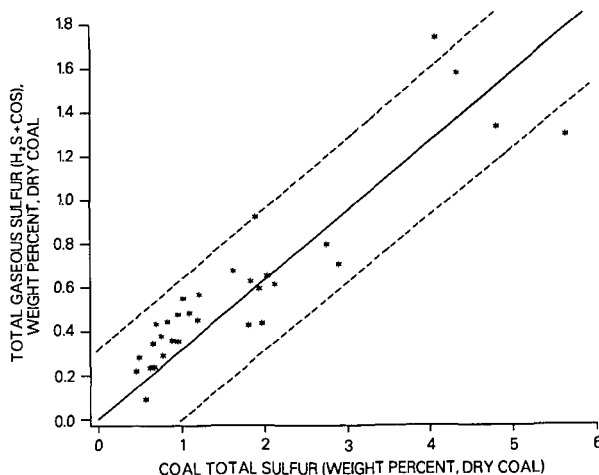
The results of this study demonstrate that the total gaseous sulfur ($H_2S + COS$) generated during coal pyrolysis can be correlated with the total coal sulfur. Furthermore, total coal sulfur could be utilized to predict the yields of H_2S or COS species individually. Correlations between the feed coal sulfur and char or tar sulfur have been obtained. The char sulfur could be correlated somewhat with the pyritic sulfur content. However, correlations between sulfur type (organic, pyritic, or sulfatic sulfur) with sulfur content in the products were generally poor. Multivariate analysis will be performed in the future to understand the role of sulfur type (e.g., pyritic, organic, or sulfatic sulfur) on their distribution.

The essence of this investigation is the development of a number of correlations for relating the distribution of coal sulfur into solid, liquid, or gaseous products occurring during pyrolysis. It is shown that about 61 percent of coal sulfur appears in the char while about 31 percent of coal sulfur appears as gaseous products when coal is pyrolyzed at a relatively low temperature ($500^\circ C$). With an increase in the peak devolatilization temperature, however, the gaseous sulfur yield increases monotonically for the Pittsburgh No. 8 coal at the expense of char sulfur.

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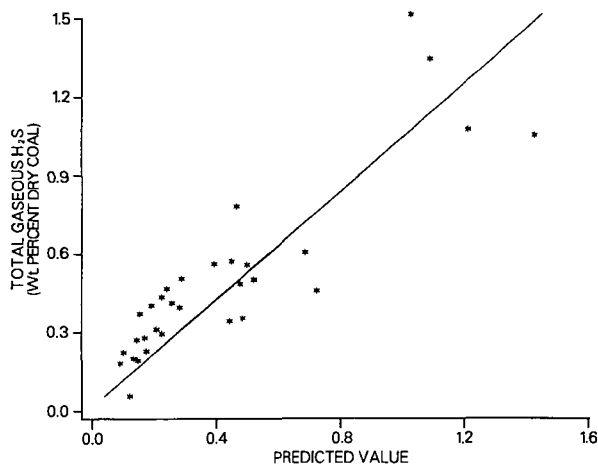
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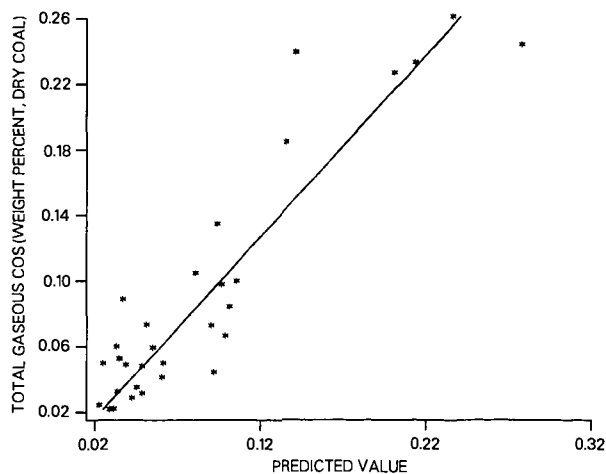
Figure 1A. The relationship between the total gaseous sulfur with the feedstock sulfur content (weight percent, dry coal). The solid line represents the regression through data. The dashed lines represent 90th percentile confidence limits for the mean predicted values.

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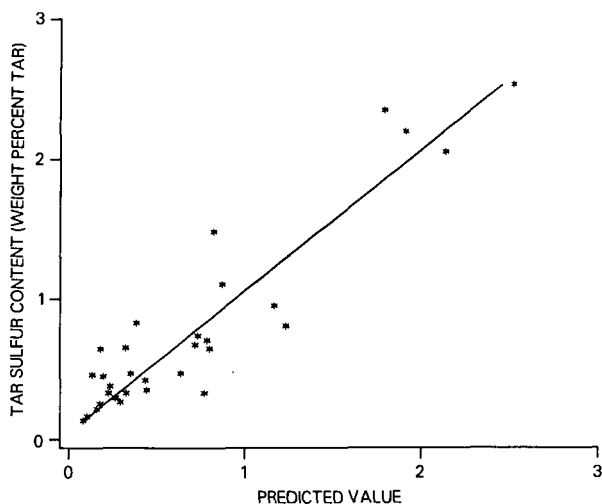
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Figure 1B. A comparison between the predicted and actual H_2S yield. The prediction was based solely on the sulfur content of the coal (weight percent, dry coal).



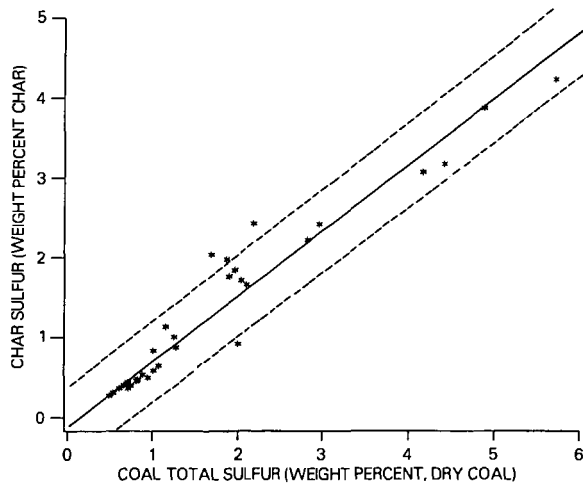
IBB-800-1C BP4

Figure 1C. A comparison between the predicted and actual COS yield. The predictions was based on feed sulfur content (weight percent, dry coal).



188-800-2A BP4

Figure 2. A comparison between the predicted and measured sulfur content of the pyrolysis tar (weight percent of tar). The prediction was based on coal sulfur (weight percent dry coal).



188-800-3A BP4

Figure 3A. The comparison between the char sulfur content (weight percent char) with the feed coal sulfur content (weight percent, dry coal). The solid line represents the regression through the data. The dashed lines represent 90th percentile confidence limits for the mean predicted values.

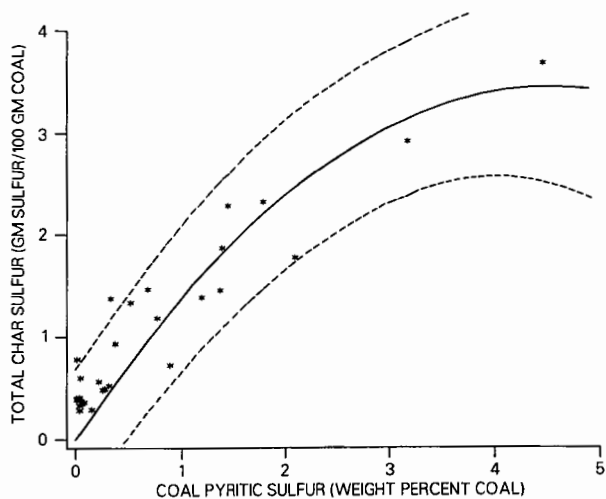


Figure 3B. A relationship between the char sulfur content (weight percent char) with the pyritic sulfur content (weight percent, dry coal). The solid represents the regression through the data. The dashed lines represent 90th percentile confidence limits for the mean predicted values.

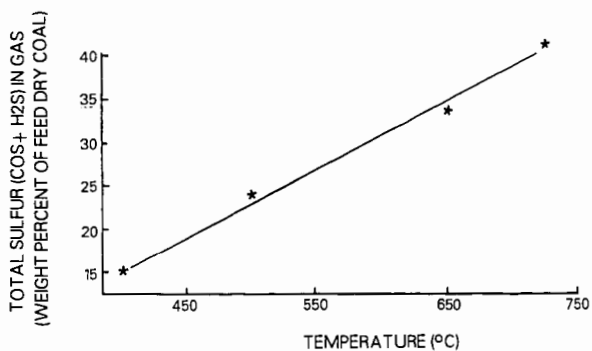
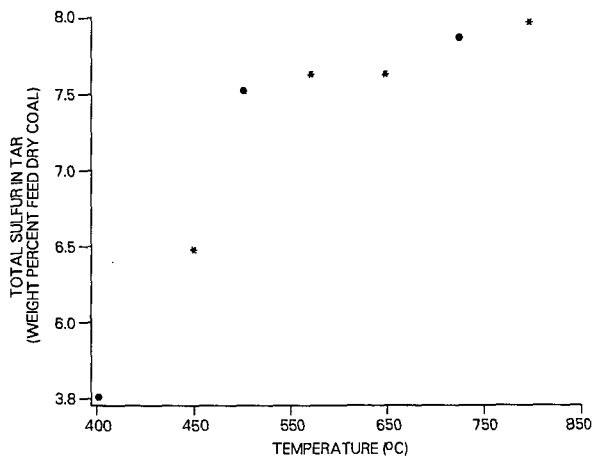
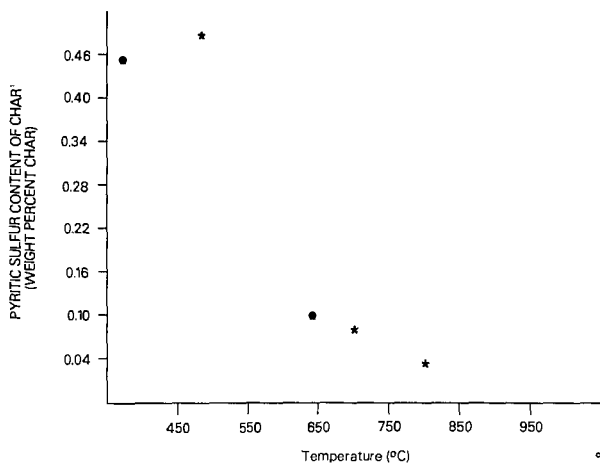


Figure 4. Influence of peak pyrolysis temperature on total gaseous sulfur yield ($\text{H}_2\text{S} + \text{COS}$) as a function of temperature.



C68-900-Z BP4

Figure 5. Influence of peak pyrolysis temperature on tar sulfur content (weight percent of tar).



C68-09A-A BP1

Figure 6. Pyritic sulfur content in char prepared at various peak temperatures.

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